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Coordination Compounds of Rare-Earth Metal Thiocyanates

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Abstract—The data on homo- and heteroleptic molecular and ionic Sc, Y, and lanthanide thiocyanates are systematized and generalized. The influence of the metal cation, its coordination number, and the ligand environment on the formation of the coordination sphere and stereochemistry of rare-earth metal thiocyanates is studied. The bibliography consists of 62 references.

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INTRODUCTION

In the so-called long-period form of the periodic table, Group III includes the rare-earth metals: Sc, Y, La, and lanthanides. The most stable oxidation state of these metals is +3, and the ion radius of the three-charged cations in the octahedral environment is 0.83, 1.06, and 1.22 Å for Sc, Y, and La, respectively. Further, along the lanthanide series, the ion radius varies within up to 1 Å [1]. The large ion radius of rare-earth metals in combination with the predominantly electrostatic nature of metal–ligand binding results in the formation of compounds with the coordination number up to 9 and higher and stereochemical variety of the formed compounds [2, 3].

The coordination compounds of rare-earth metals have characteristic photophysical and magnetic properties, predetermining prospects of their use in magnetic and optical devices [4–9], sensor systems [10], biological analysis [11–13], medical diagnostic apparatus [14–16], etc.

Three-charged cations of rare-earth metals are arranged in a series of hard acids (according to the Hard and Soft Acid Base (HSAB) theory). They prefer ligands with hard donor atoms: N, O, or acido ligands, namely, halides, pseudo-halides, among which the thiocyanate ion (NCS^-) occupies a special place. The specific features of the structure, charge distribution, and coordination possibilities of the NCS^- anion were considered in detail [17]. The triatomic linear thiocyanate ion is an ambidentate ligand and can be terminal in the case of the monodentate coordination mode or bridging for binding to the metal cation simultaneously through the sulfur and nitrogen atoms, M—NCS—M. The largest size of the hard donor nitrogen atom and a nearly linear configuration of the anion make it possible to obtain thiocyanate forms of rare-earth metals with the coordination number ≥ 6. Unlike transition metal compounds, thiocyanate compounds of rare-earth metals have no rich bibliography. A sufficiently complete literature analysis of this scientific direction [18] considers the homoleptic thiocyanate compounds and, to a lower extent, the heteroleptic thiocyanate derivatives of rare-earth metals. As a rule, thiocyanate metal compounds are synthesized using the metathesis reaction between hydrated salts (chlorides or nitrates) of the corresponding metals and KNCS in alcoholic solutions [19]. A low toxicity of the thiocyanate anion predetermines its use in pharmacology, and the variety of easy binding with metal ions finds use in biochemical studies. The present interest in rare-earth metal thiocyanates is related to the real and promising applications in extraction, sensor devices, and diagnostics and treatment of oncological problems. In the latter case, exciting results were obtained for the lanthanum thiocyanate complex with phenanthroline. This complex was in vitro and in vivo tested as an antitumor drug exhibiting cytotoxicity toward a series of cancer cells [20].

This review is not a detailed and comprehensive compilation of the modern data on the rare-earth metal thiocyanates. The main tendencies and features of the coordination compounds of three-charged cation thiocyanates in both homoleptic and heteroleptic compounds with mono- and polydentate N- and O-donor ligands are considered. An attention was concentrated on the influence of the complexing cation and ligand environment on the formation of molecular and ionic forms and on an analysis of stereochemical features of the known thiocyanate compounds.

MOLECULAR COORDINATION COMPOUNDS

Complexes with O-donor ligands. The formation of the thiocyanate complexes with M = Y, La, Nd, Tb,

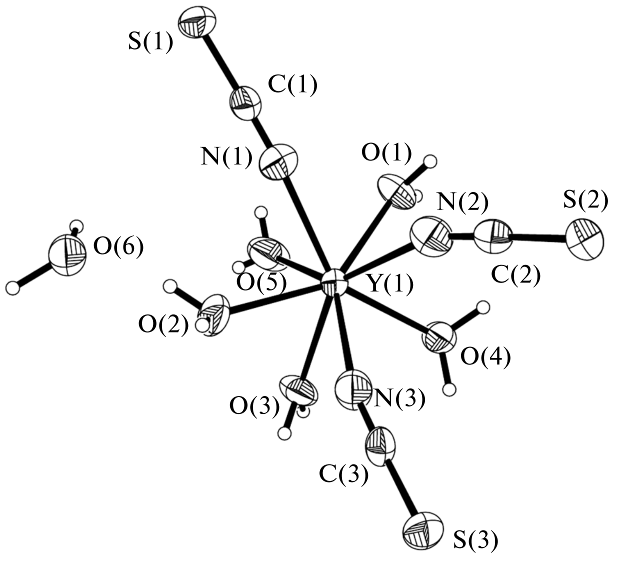

Fig. 1. Molecular structure of complex $[Y(H_2O)_5(NCS)_3] \cdot H_2O$.

Ho, Tm, and Yb in a solution of dimethylformamide (DMF) was considered in 1992 [21]. The constants of formation were calculated for a series of complexes $[M(NCS)_n]^{3-n}$ (n = 1–3) with the N-coordination of the thiocyanate anion. The obtained thermodynamic parameters depend weakly on the complexing atom, which was due to the retention of the geometry of the complexes in a solution for the whole series of the studied rare-earth metals.

The hydrated thiocyanates $M(NCS)_3 \cdot 6H_2O$ (M = Y, Sm, Gd, Yb) were obtained by the multistage synthesis using rare-earth metal oxide, $Ba(OH)_2 \cdot 8H_2O$, a solution of H_2SO_4, and NH_4NCS [22]. An analysis of the data on the low-temperature (13–300 K) heat capacity and thermodynamic characteristics of all studied compounds showed no anomalies. The X-ray diffraction study of hydrate $Y(NCS)_3 \cdot 6H_2O$ established [23] that the thiocyanate was a coordination compound of the formula $[Y(H_2O)_5(NCS)_3] \cdot H_2O$ (**I**), whose coordination sphere was formed of five water molecules and three acido ligands coordinated through the nitrogen atom. The coordination number of yttrium is 8, and the coordination mode is YO_5N_3. The crystal structure consists of the molecular complex and crystallization water molecules (Fig. 1). The structure contains 12 hydrogen atoms, and all of them form hydrogen bonds. Sulfur atoms act as acceptors in nine hydrogen bonds, the O atom of the water molecule of the hydrate acts as an acceptor in two hydrogen bonds, and the N atom acts as an acceptor in one hydrogen bond. The complexes and water molecules of the hydrate joined by hydrogen bonds form a framework in the structure. Thiocyanates $[M(H_2O)_5(NCS)_3] \cdot H_2O$ with M = Eu (**III**) and Tb (**III**) were isolated from aqueous solutions of HNCS in which the corresponding oxides M_2O_3 interacted with thiocyanic acid [24]. Compounds **I–III** are isostructural. In the IR spectra of these complexes, the characteristic band ν(CN) consists of two components with 1985, 1970; 2095, 2077; and 2100, 2085 cm^{-1} for **I**, **II**, and **III**, respectively, which is determined by the nonequivalent position of the thiocyanate groups in the structure, and the frequency shift is consistent with an increase in the number of the rare-earth metal. The thermal decomposition of compounds **I–III** is interesting: it starts from ~65°C and some thiocyanate anions are removed during the further thermal destruction in a range of 200–300°C. Unlike yttrium and terbium thiocyanates, the thermal decomposition of europium thiocyanate in an inert atmosphere proceeds with the reduction of the three-charged europium cation [24]. Aquathiocyanates **I–III** are stable at room temperature, are not hydrolyzed, retain structural features for several years, and are successful precursors for the synthesis of heteroleptic compounds with organic ligands.

Water molecules in the coordination sphere of rare-earth metal thiocyanates are easily replaced by monodentate donor ligands. Molecular complexes $[Ln(NCS)_3L_5]$ (Ln = La, Ce, Pr, Nd, Sm, Eu, and Tb; L is 1,3-dithiane-1-oxide) were synthesized [25] by the reaction of lanthanide thiocyanates with L in an ethanol solution. The X-ray diffraction analysis for $[Tb(NCS)_3L_5]$ showed that ligand L was coordinated through the oxygen atom in a square antiprism, the NCS^- anion was coordinated through the nitrogen atom, the coordination number was 8, and the coordination mode was LnO_5N_3 similarly to aqua complexes **I–III**.

However, in the case of monodentate tetrahydrofuran (THF), dimeric forms $[M(NCS)_3(THF)_4]_2$ (**IV**) (M = Y, La, Nd, Sm, Dy, Ho) are formed [26] in which the molecular complexes with a coordination number of 8 are linked by two M–NCS–M bridges. The same dimeric structure **IV** was established for the neodymium, europium, and erbium complexes [27]. A distorted antiprism in structures **IV** is Y-shaped for three M–N bonds, the terminal and bridging nitrogen atoms are most tightly arranged, and three SMN angles are T-shaped. The ambidentate character of the thiocyanate ion is unusual for hard rare-earth metal cations, which is possibly due to the synthesis conditions of complexes **IV** unstable in air and readily composed. The dimers were obtained by the oxidation of the rare-earth metals with mercury thiocyanate $Hg(NCS)_2$ in a THF solution under an inert atmosphere using a glove box or Schlenk technique. In the case of chelating dimethoxyethane (Dme), monomeric complexes $[M(NCS)_3(Dme)_3]$ (M = La, Nd) were also obtained using oxidation with mercury thiocyanate [26]. In these complexes, the rare-earth metal is coordinated by six oxygen atoms and three nitrogen atoms (coordination number 9). The NCS ligands in the lanthanum complex have a *mer* conformation and one *trans*-NMN angle. Two *trans*-NMN angles are observed in the neodymium complex. The complexing agent affects not only the geometry of the coordination sphere. Dimeric complexes $[Ln(NCS)_3(Dme)_2(\mu\text{-}Dme)_{0.5}]_2$ (Ln = Eu, Dy, Er) were obtained [26] in which the lanthanide cation was coordinated by three NCS^- anions and five oxygen atoms that were presented by two chelating and one bridging Dme molecules, and the coordination number of the cation decreased to 8. The shortening of the Ln–N and Ln–O bonds with an increase in the number of lanthanide in the series Eu, Dy, and Er due to lanthanide contraction was observed in these dimers.

The introduction of polydentate O-donor ligands into the coordination sphere of the rare-earth metal thiocyanates enhances the stability of the compounds. Polyatomic alcohols and macrocycles usually act as these ligands. The X-ray diffraction data on the rare-earth metal complexes with tri-, tetra-, penta-, and hexa(ethylene glycols), which form O-polydentate spheres similar to crown ethers, and with various anions (Cl^-, SCN^-, NO_3^-) were systematized [28]. For the thiocyanate complexes, the chain length of polyatomic alcohol determines the composition of the coordination sphere. In the case of tetra(ethylene glycol) (EO4), complexes $[M(NCS)_3(H_2O)(EO4)]$ (M = La, Ce, Nd, Sm, Gd, Y) are formed. For penta(ethylene glycol) (EO5), the coordination sphere of the rare-earth metal contains no water molecules: $[M(NCS)_3(EO5)]$ (M = La, Ce, Nd, Sm, Gd, Y, Yb). Regardless of the chain length of glycol, the coordination number of the cation is 9, and an increase in the coordination number to 9 in the complexes with EO4 (pentadentate ligand) is attained by the coordination of one water molecule.

The ability of macrocycles and crown ethers to the *endo* (inner-sphere) and *exo* (out-of-sphere) coordination of cations (or their complexes) depends on the compatibility of partners, conditions of interaction, and solvent. Monomeric complexes $[Ln(NCS)_3(18C6)] \cdot THF$ (Ln = La, Nd, Dy, Yb) were synthesized [29] using the 1,4,7,10,13,16-hexaoxocyclooctadecane macrocycle (18C6) as a polydentate O-donor ligand and dimeric complexes **IV**. The complexes are isostructural, and the coordination number is 9 due to three nitrogen atoms of the anions and six oxygen atoms of the macrocycle. In these complexes, changes in the Ln–N and Ln–O bond lengths are determined by steric hindrances from lanthanide contraction and are supplemented by the coordination of 18C6. The ν(CN) band in the IR spectra increases monotonically from 2038 to 2057 cm^{-1} on going from La to Yb according to an increase in the number of Ln. Unlike precursors **IV**, the complexes are not hygroscopic and are stable in air.

The use of aquathiocyanates **I–III** as precursors in the synthesis with 18C6 revealed a remarkable role of supramolecular aggregation in the synthesis of the compounds with the *exo*- or *endo*-coordinated macrocycles. The reaction of **I** with 18C6 in MeOH and EtOH solutions affords associate $[Y(H_2O)_4(NCS)_3] \cdot 1.5(18C6)$ (**V**) [23]. Although compound **V** was isolated from the solution with the molar ratio **I** : 18C6 = 1.3, this ratio is 1.5 in the obtained solvate **V**. Interestingly, the initial yttrium complex had to "sacrifice" one coordinated water molecule to form associate **V**. The complex in associate **V** has the composition $[Y(H_2O)_4(NCS)_3]$ and coordination number 7. Structure **V** contains molecular complexes $[Y(H_2O)_4(NCS)_3]$ and 18C6 molecules (Fig. 2). The coordination polyhedron of the yttrium atom is a one-capped trigonal prism. A higher electronegativity of oxygen compared to that of sulfur results in the situation where the O–H···S hydrogen bonds are not formed in structure **V** and the oxygen atoms of 18C6 are acceptors in all hydrogen bonds. The central macrocycle of the fragment (Fig. 2) has the most favorable *gauche*(OCCO)–*trans*(COCC) conformation and is localized at the inversion center, which provides the possibility of formation of three hydrogen bonds with water molecules of one complex. The remaining five hydrogen atoms of three water molecules can theoretically form five hydrogen bonds with the oxygen atoms of the second 18C6 molecule, whose conformation, for this purpose, should be close to the conformation of the ether in the sandwich complexes $M(18CK6)_2$. A comparison of the characteristic bands in the IR spectra of compounds **I** and **V** shows the most noticeable change in the composition of the coordination sphere and coordination number of the complexing agent in the shift of the ν(CN) band of the coordinated NCS groups and the $\delta(H_2O)$ band of the water molecules. The appreciable decrease (50 cm^{-1}) in the $\delta(H_2O)$ frequency for compound **V** compared to compound **I** is related to different natures of the hydrogen atoms in the hydrogen bonds O_w–H···O and O_w–H···S.

The solvent effect on the interaction of compound **I** with 18C6 was studied [30]. The complexes with the inner-sphere coordination of crown ether, $[Y(18C6)(NCS)_3]$ (**VI**) and $[Y(18C6)(NCS)_3] \cdot nA$ ($A = CH_3CN$, THF, 18C6) (**VII**), were obtained from solvents of different nature (acetonitrile, THF, ethyl acetate, *iso*-PrOH) under usual conditions (room temperature and moisture content). In compounds **VII**, the structures of the complexes are the same: two nitrogen atoms of ligands NCS are arranged at one side from the mean plane of 18C6, the third atom is located at another side from this plane (Fig. 3), and the polyhedron can be described as a three-capped trigonal prism. A specific feature of the studied

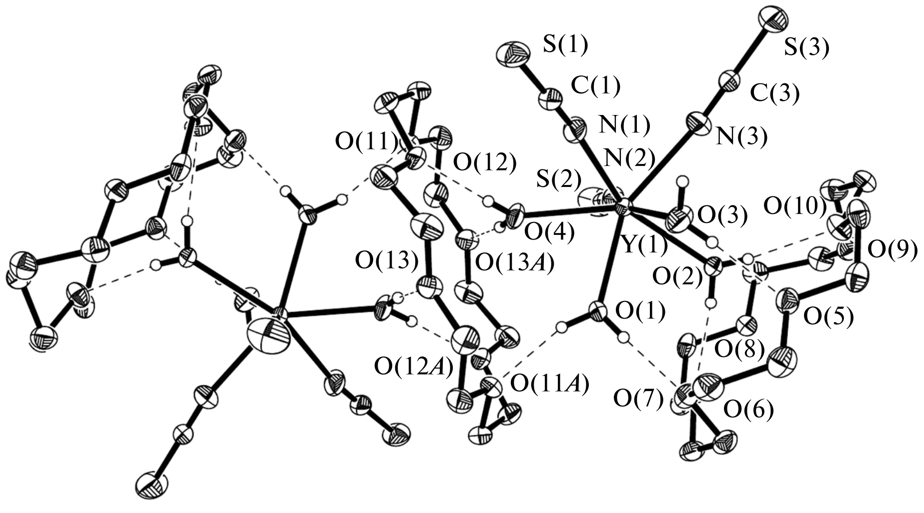

Fig. 2. Fragment of the structure of ensemble $[Y(H_2O)_4(NCS)_3] \cdot 1.5(18C6)$.

interactions is the complete dehydration of the internal sphere of aquathiocyanate complex **I** and also the everywhere absence of a solvate with the out-of-sphere water molecule, which made it possible to perform the full dehydration of complex $[Y(H_2O)_5(NCS)_3] \cdot H_2O$ under mild conditions. In anhydrous compounds **VI** and **VII**, yttrium is coordinated by six oxygen atoms of the macrocycle and three nitrogen atoms of the acido ligand (coordination number 9). An easy transition from the inner-sphere coordination of the macrocycle to the out-of-sphere coordination with the formation of compound **V** (and backward) upon the replacement of acceptor solvents by donor solvents was revealed for compounds **VI** and **VII** [30]. Aquathiocyanates **II** and **III** react with 18C6 in a solution of MeOH or EtOH to form moisture-resistant anhydrous polymorphous modifications $[M(18C6)(NCS)_3]$ (M = Eu, Tb) with the *endo* coordination of the macrocycle (Fig. 4) in which the complexing agent has a coordination number of 9. Regardless of the initial ratio 18C6 : Eu, crystals of solvate $[Eu(18C6)(NCS)_3] \cdot 0.5(18C6)$ similar to the solvate of yttrium thiocyanate (Fig. 3) were identified in the mother liquors in each synthesis [24]. The structural variety of complexes $[M(18\text{-crown-}6)(NCS)_3] \cdot x(18C6)$ ($x = 0$ (Eu, Tb), $x = 0.5$ (Y, Eu), $x = 1$ for Y) is caused by the absence in these crystals of significant secondary interactions that could provide the mutual orientation of adjacent molecules upon crystallization. It is most likely that the isolation of this or another phase depends on minimum changes upon crystallization: in the temperature and in the presence of microimpurities and defects on the glassware surface. In the case of Eu and Tb, water molecules in the aquathiocyanates are replaced by the macrocycle in protolytic solvents, methanol and ethanol, unlike yttrium for which the formation of anhydrous forms was detected only in aprotic solvents. Perhaps, this is due to a change in the $M{-}OH_2$ binding on going along the series Y–Eu–Tb: in the case of yttrium thiocyanate, coordinated H_2O molecules prefer out-of-sphere coordination in alcoholic solutions. Compounds $[M(18C6)(NCS)_3]$ (Y, Eu, Tb) are thermally stable up to 300°C due to the macrocyclic effect. The study of the luminescence properties of the europium and terbium complexes showed that the aquathiocyanates exhibited photoluminescence characteristic of Eu^{3+} and Tb^{3+} ions upon direct excitation. The full quenching of the luminescence of the rare-earth metal ions in anhydrous complexes $[M(18C6)(NCS)_3]$ (M = Eu, Tb) was quite unexpected [30].

Complexes with N-donor ligands. Classical N-donor bidentate neutral ligands, 2,2'-bipyridine (Bipy) and 1,10-phenanthroline (Phen), were first used for the synthesis of coordination compounds of lanthanide thiocyanates [31, 32]. In these works, rare-earth metal thiocyanates were obtained by the metathesis reactions of hydrated rare-earth metal chlorides (nitrates) and KNCS in alcoholic solutions. The isolated compounds were identified according to the data on elemental analysis, IR spectroscopy, and decomposition temperatures, which did not allow unambiguous conclusions about the composition of the first coordination sphere and the coordination mode of NCS^-. This method of the synthesis of thiocyanates in solution is efficiently used presently. The data on thiocyanates of various stoichiometry ($Ln(Bipy)_x(NCS)_3(H_2O)_y$ for Ln = La, Pr, Nd, Sm, and Er) were published without a structural information [33].

Structurally characterized praseodymium thiocyanate $Pr(Bipy)_3(NCS)_3$ **(VIII)** was obtained from an

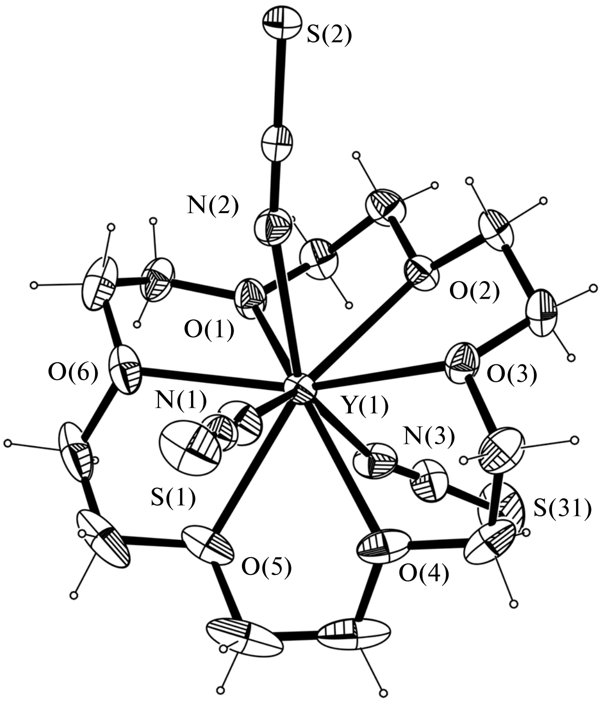

Fig. 3. Structure of complex [Y(18C6)(NCS)$_3$] · 0.5(18C6).

ethanol solution of praseodymium nitrate hydrate and KNCS [34]. In monomeric compound **VIII**, the cation is bound to three N-coordinated anions and three Bipy molecules, its coordination number is 9, the coordination sphere consists of nitrogen atoms only, and the coordination mode is PrN$_9$. Ethanol solvates [Ln(Phen)$_3$)(NCS)$_3$] · EtOH (Ln = Pr, Nd) (**IX**) were also obtained from Ln nitrate salts and KNCS [35]. Solvates **IX** are isomorphic and isostructural, the coordination number of the cation is 9, and the coordination mode LnN$_9$ is similar to that in complex **VIII** [34]. In the crystal structures [Ln(Phen)$_3$(NCS)$_3$] · EtOH, solvate molecules EtOH are involved in hydrogen bonding in which the OH groups act as donors of the hydrogen bond and simultaneously as acceptors through the oxygen atom.

Complex [La(Phen)$_3$(NCS)$_3$] (**X**) [36] was synthesized using a described method [31], and the X-ray diffraction data confirmed the coordination of the thiocyanate anions through the nitrogen atom, the coordination number of the cation equal to 9, and almost linear coordinated ligands NCS$^-$ (average angle NCS 178.5°). The ν(CN) absorption band is observed at 2052 cm^{-1} in the IR spectra. Since complex **X** is a promising anticancer drug (KR772), the state of complex *X* in aqueous solutions and its interaction with a series of biomolecules were studied [36].

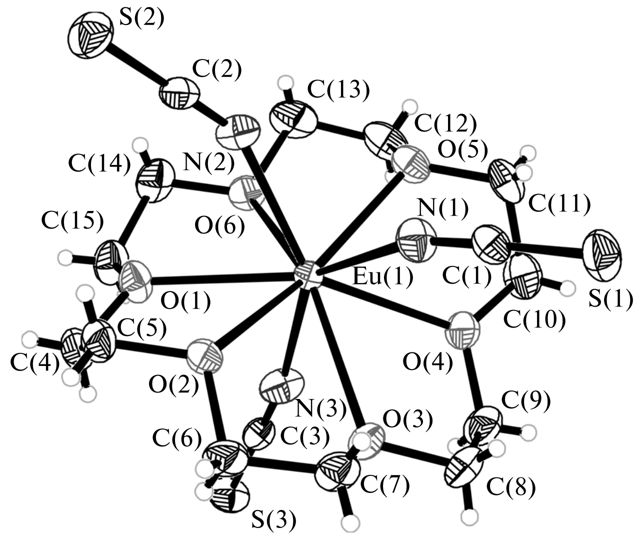

Fig. 4. Monoclinic modification of structure [Eu(18C6)(NCS)$_3$].

The tridentate N-donor ligand, 2,2':6',2''-tetrapyridine (Terpy), with Ln thiocyanates also forms complexes having a coordination number of 9 and coordination mode LnN$_9$, [Ln(Terpy)$_2$(NCS)$_3$] (Ln = Pr, Nd) (**XI**) and [Nd(Terpy)$_2$(NCS)$_3$] · 2EtOH (**XII**) [35]. Complexes **IX**, **XI**, and **XII** were isolated from ethanol solutions after the nitrate anions in the hydrated Ln salts were replaced by anions NCS$^-$. In the molecular structures, the Ln–NCS distances are shorter than Ln–N(Phen, Terpy) and all Nd–ligand bonds are shortened compared to the Pr–ligand bonds due to lanthanide contraction. In all considered complexes, three thiocyanate ligands have a meridional configuration with two pseudo-axial groups and one equatorial group and all NCS$^-$ ligands are linear. The structural differences observed for the pseudo-axial and equatorial Ln–N(C) bonds in complexes **XI** and **XII** with Terpy and in complex **IX** with Phen are due to steric interactions near the metallic center caused by the predominant ionic and undirected binding of the rare-earth metals with the ligands. In all complexes **IX**, **XI**, and **XII**, the thiocyanate groups are involved in hydrogen bonds C–H···S and the aromatic ligands participate in the π–π interaction [35].

Complexes [M(NCS)$_3$(C$_{22}$H$_{26}$N$_6$)] with the hexadentate N-donor macrocyclic ligand, 2,7,13,18-tetramethyl-3,6,14,17,23,24-hexaazatricyclo[17.3.1.1][tetracosa-1(23),2,6,8(24),9,11,13,17,19,21-decaene-N^3,N^6,N^{14},N^{17},N^{23},N^{24} (C$_{22}$H$_{26}$N$_6$), and M = Y and Eu were synthesized and studied [37]. It was found that the crystals contained two types of complexes with a coordination number of 9 and different conformations of the macrocycle. In the β form of complex [Eu(NCS)$_3$(C$_{22}$H$_{26}$N$_6$)] [38], the coordination geometry

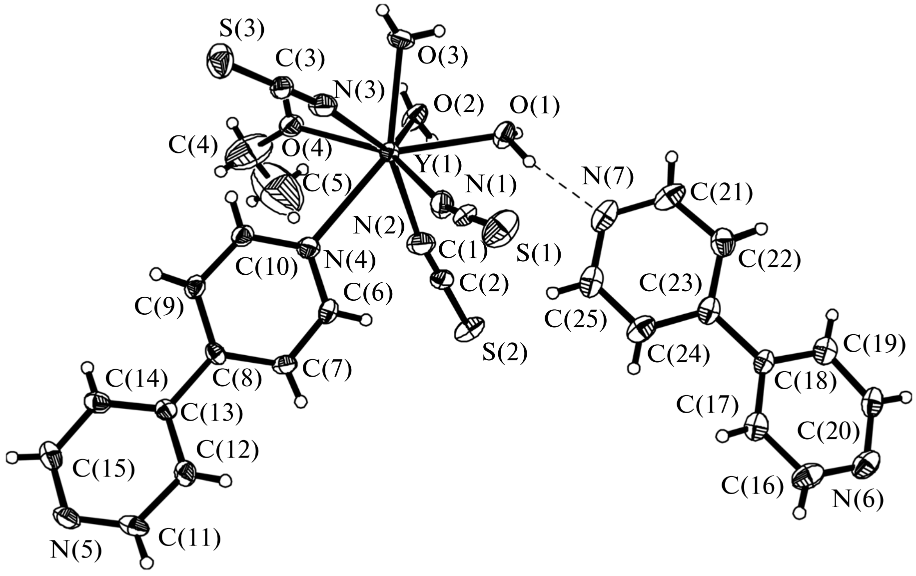

Fig. 5. Fragment of structure $[Y(H_2O)_3EtOH(4,4'\text{-}Bipy)(NCS)_3] \cdot (4,4'\text{-}Bipy)$.

is similar to the α form and the cation exists in the 18-membered plane linked with six nitrogen atoms (coordination number 9). The lanthanum complex, $[La(C_{24}H_{30}N_6)(NCS)_3(H_2O)] \cdot H_2O$, was obtained by the template synthesis, the macrocyclic ligand $C_{24}H_{30}N_6$ is a derivative of $C_{22}H_{26}N_6$ in which each side diimine chain has a methyl substituent, and the coordination number of the cation in the complex is 10 [39].

The macroazacyclic ligand Tdco (1,7,10,16-tetraoxa-4,13-diazacyclooctadecane) forms complexes $[Ln(NCS)_3(Tdco)]$ (Ln = Eu, Yb) with the coordination number of Ln equal to 9. The coordination sphere of Ln consists of three N-acido ligands, two nitrogen atoms, and four oxygen atoms of the macrocycle, the coordination mode is LnN_5O_4, and the NCS^- anions are arranged at different sides from the Tdco plane [40].

Complex formation with ditopic 4,4'-bipyridine (4,4'-Bipy) proceeds in somewhat different manner, since 4,4'-Bipy can (1) accomplish ditopicity by the formation of bridges between the metallic centers, (2) act (in the protonated form) as a counterion, (3) be a guest molecule if it is located in cavities of the structure, or (4) be coordinated via the monodentate mode by the metal ion. The reaction of yttrium thiocyanate **I** with 4,4'-Bipy was studied [41]. This reaction resulted in the isolation of $[Y(H_2O)_3EtOH(4,4'\text{-}Bipy)(NCS)_3] \cdot (4,4'\text{-}Bipy)$ (**XIII**) from ethanol and $\{\mu\text{-}(4,4'\text{-}Bipy)[Y(NCS)_3(H_2O)_3]_2\} \cdot 3(4,4'\text{-}Bipy) \cdot 2(\textit{iso}\text{-}PrOH)$ (**XIV**) from *iso*-propanol. Compound **XIII** with the ratio 4,4'-Bipy : Y = 2 was isolated from ethanol solutions in which the initial 4,4'-Bipy : Y ratio varied from 1 to 4, and an increase in the ratio decreased the purity of the product. According to the X-ray diffraction data, pure **XIII** was obtained from a solution with the ratio Bipy : Y = 2, and a low (~50%) yield was due to a high solubility of **XIII** in ethanol. In ensemble **XIII**, one of the 4,4'-Bipy molecules is coordinated through the monodentate mode, while another molecule is solvate. It is interesting that it is 4,4'-Bipy which is the solvate molecule rather than protolytic molecules H_2O or EtOH. Structure **XIII** is formed by the complex molecules and solvate molecules 4,4'-Bipy (Fig. 5). Six of seven hydrogen atoms of the coordinated molecules H_2O and EtOH are involved in the formation of hydrogen bonds O–H···N(S). The combined action of six hydrogen bonds joins the structural units into two mutually penetrating 3D networks. Ensemble **XIV** was obtained by two methods: by the treatment of compound **XIII** with *iso*-propanol or by the direct interaction of yttrium thiocyanate with 4,4'-Bipy in a solution of *iso*-PrOH. The formation of compound **XIV** can be considered as the dimerization of compound **XIII**. Upon the dimerization, coordinated EtOH leaves the coordination sphere and monodentate 4,4'-Bipy becomes a bridging linker in compound **XIV**. The solvate shell of compound **XIV** is noteworthy: in the presence of two *iso*-PrOH molecules, the supramolecular ensemble contains now already three 4,4'-Bipy molecules. Structure **XIV** contains centrosymmetric dimeric molecular complexes (Fig. 6) and solvate molecules 4,4'-Bipy and *iso*-PrOH. An *iso*-PrOH molecule is bound to the complex by two hydrogen bonds as a donor with the hydrogen atom of the coordinated H_2O molecule and as an acceptor in the O–H···S hydrogen

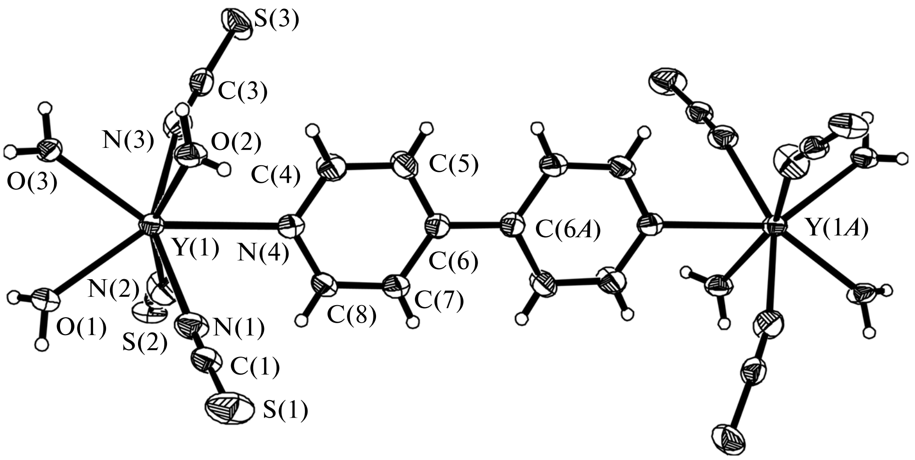

Fig. 6. Fragment of structure {μ-(4,4'-Bipy)$[Y(NCS)_3(H_2O)_3]_2$} · 3(4,4'-Bipy) · 2(*iso*-PrOH).

bond. Solvate molecules 4,4'-Bipy join the associates into two mutually penetrating 3D networks. It should be especially mentioned that the formation of supramolecular ensemble **XIV** is accompanied by a change in the coordination number of yttrium: 8 for **I** and 7 for **XIV**. The photoluminescence characteristics of compounds **XIII–XIV** determined in [41] indicate that 4,4'-Bipy participates in the energy transfer, which is manifested as a shift of the emission maxima to the long-wavelength range. The formation of supramolecular ensembles is also characteristic of ditopic 4,7-phenanthroline (4,7-Phen), for example, the interaction of alcoholic solutions of compound **I** and 4,7-Phen in the presence of an aqueous solution of HNCS gave ensemble $[Y(H_2O)_5(NCS)_3]$ · 2(4,7-Phen) · $2(H_2O)$ without a contact of 4,7-Phen with yttrium, and the molecules of the condensed N-heterocycle is joined in the structure into stacks due to the stacking interaction [42].

The structurally characterized molecular coordination compounds of the rare-earth metals are collected in the table. Almost all compounds, except for nos. 3, 5, and 21, are monomers. Dimerization in compound no. 3 occurs due to the NCS bridges, which accomplish the rare (for rare-earth metals) coordination through both the nitrogen atom and sulfur atom. In compound nos. 5 and 21, the L- and N-donor ligands act as bidentate-bridging ligands. All compounds, regardless of the preparation method, contain three acido ligands in the coordination sphere. Rare-earth metals with monodentate ligands in heteroleptic forms almost always have the coordination number 8, whereas the coordination number increases to 9 and even to 10 (no. 18) for polydentate ligands. In the case of chelating N-donors (Bipy, Phen, Terpy), the coordination mode LnN_9 consists of nitrogen atoms only. Three yttrium compounds (nos. 9, 21, and 22 in the table) have a coordination number of 7 in supramolecular associates.

IONIC COORDINATION COMPOUNDS

Homoleptic coordination compounds. Homoleptic thiocyanate anions $[M(NCS)_6]^{3-}$ in complexes $Q_3[M(NCS)_6]$ for M = Sc, Y, and Ln were subjected to a series of spectral and structural studies [43–48]. The molecular structure of complex $[Bu_4N]_3[Y(NCS)_6]$ obtained from an ethanol solution of yttrium chloride and Bu_4N · NCS was studied using EXAFS spectroscopy, the data of which were confirmed by quantum-chemical calculations (DFT) [45]. The obtained parameters are consistent with the values for similar complex $[Er(NCS)_6]^{3-}$, whose structure was determined by X-ray diffraction analysis [46]. The anions are symmetrical octahedral with the N-coordinated linear thiocyanate anions, and all YNS and NCS angles are 180°. The state of the complex in an acetonitrile solution was also studied by the NMR method [45]. The $^{13}C\{^1H\}$ NMR spectrum exhibits a well resolved signal of NCS^- at 135.1 ppm characteristic of the thiocyanate complexes with the N-coordination of the NCS^- anions. In complex $[Bu_4N]_3[Nd(NCS)_6]$, the acido ligands coordinated through the nitrogen atom form a distorted octahedral configuration, and an electrostatic interaction is observed between the out-of-sphere cations $[Bu_4N]^+$ and anions $[Nd(NCS)_6]^{3-}$ [44]. Complexes $[Bu_4N]_3[Ln(NCS)_6]$ (Ln = Eu, Gd, Dy) were obtained by the interaction of equivalent amounts of lanthanide chloride and KNCS with three equivalents of Bu_4N · NCS in ethanol [48]. The obtained salts of Eu, Gd, and Dy are isostructural between each other and isostructural to the erbium analog [46], and the metal cation is octahedrally coordinated by six thiocyanate anions through the nitrogen atom. The changes in bond lengths of these complexes

Molecular thiocyanate compounds of rare-earth metals

Compound*	Rare-earth metal	Coordination mode	Coordination number	Literature
$[M(H_2O)_5(NCS)_3] \cdot H_2O$	Y, Eu, Tb	MN_3O_5	8	[23, 24]
$[Ln(NCS)_3L_5]$	La, Ce, Pr, Nd, Sm, Eu, Tb	LnN_3O_5	8	[25]
$[M(NCS)_3(THF)_4]_2$	Y, La, Nd, Sm, Dy, Ho	MN_3O_4S	8	[26]
	Nd, Eu, Er	MN_3O_4S	8	[27]
$[M(NCS)_3(Dme)_3]$	La, Nd	MN_3O_6	9	[26]
$[Ln(NCS)_3(Dme)_2(\mu\text{-}Dme)_{0.5}]_2$	Eu, Dy, Er	LnN_3O_5	8	[26]
$[M(NCS)_3(H_2O)(EO4)]$	La, Ce, Nd, Sm, Gd, Y	MN_3O_6	9	[28]
$[M(NCS)_3(EO5)]$	La, Ce, Nd, Sm, Gd, Y, Yb	MN_3O_6	9	[28]
$[Ln(NCS)_3(18C6)] \cdot THF$	La, Nd, Dy, Yb	LnN_3O_9	9	[29]
$[Y(H_2O)_4(NCS)_3] \cdot 1.5(18C6)$		YN_3O_4	7	[23]
$[M(18C6)(NCS)_3] \cdot 0.5(18C6)$	Y, Eu	MN_3O_6	9	[24, 30]
$[M(18C6)(NCS)_3]$	Y, Eu, Tb	MN_3O_6	9	[24, 30]
$[Pr(Bipy)_3(NCS)_3]$		PrN_9	9	[34]
$[Ln(Phen)_3(NCS)_3] \cdot EtOH$	Pr, Nd	LnN_9	9	[35]
$[La(Phen)_3(NCS)_3]$		LaN_9	9	[36]
$[Ln(Terpy)_2(NCS)_3]$	Pr, Nd	LnN_9	9	[35]
$[Nd(Terpy)_2(NCS)_3] \cdot 2EtOH$		NdN_9	9	[35]
$[M(NCS)_3(C_{22}H_{26}N_6)]$	Y, Eu	MN_9	9	[37]
$[La(C_{24}H_{30}N_6)(NCS)_3(H_2O)] \cdot H_2O$		LaN_9O	10	[39]
$[Ln(NCS)_3(Tdco)]$	Eu, Yb	LnN_5O_4	9	[40]
$[Y(H_2O)_3EtOH(4,4'\text{-}Bipy)(NCS)_3)] \cdot (4,4'\text{-}Bipy)$		N_4O_4	8	[41]
$\{\mu\text{-}(4,4'\text{-}Bipy)[Y(NCS)_3(H_2O)_3]_2\} \cdot 3(4,4'\text{-}Bipy) \cdot 2(\textit{iso}\text{-}PrOH)$		YN_4O_3	7	[41]
$[Y(H_2O)_5(NCS)_3] \cdot 2(4,7\text{-}Phen) \cdot 2H_2O$		YN_3O_5	8	[42]

* L is 1,3-dithiane-1-oxide, EO6 is hexa(ethylene glycol), $C_{24}H_{30}N_6$ is dimethyl derivative of $C_{22}H_{26}N_6$, and Tdco is 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane.

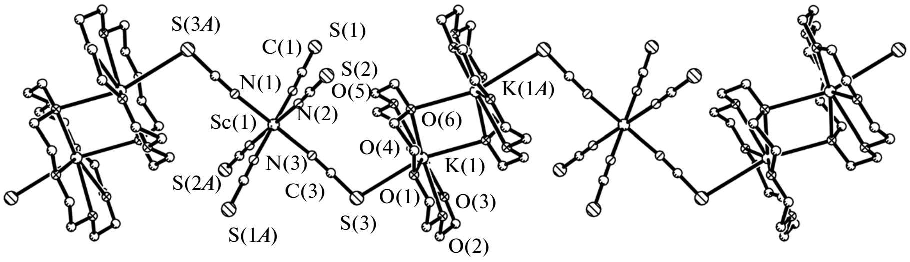

Fig. 7. Structure of the polymer chain $[K(18C6)]_2[Sc(NCS)_6]$ in compound $[K(18C6)(H_2O)_{1.66}]_{2n}\{[K(18C6)]_2[Sc(NCS)_6]\}_n \cdot n$Cl.

show a systematic change in the ion radii of the lanthanide centers.

The inclusion compounds $[Et_4N]_3[M(NCS)_6] \cdot G$ (M = Er, Yb; G is benzene, fluorobenzene, chlorobenzene, and toluene) also contain the octahedral hexathiocyanate anion (coordination number 6) [49]. These solvates are fairly stable at room temperature for several weeks. The thermoanalytical study showed that all molecules of G were removed within a range of 80–90°C and the further degradation of the complexes was of the same type.

The stabilization of the octahedral anions $[M(NCS)_6]^{3-}$ for the rare-earth metals is also observed in the presence of cations $[Q(18C6)]^+$ (Q = Na, K). The "recognition" of the anionic complexes $[M(NCS)_6]^{3-}$ by the $[Q(18C6)]^+$ cations was especially pronounced in the case of scandium thiocyanates. The systems differed in nature of the solvent (EtOH, THF, CH_3CN, *iso*-PrOH), initial scandium compound (chloride, hydroxo dimer), and used thiocyanate salt (Na, K) and gave compounds in which the NCS : Sc ratio was 6, although the initial ratio did not exceed 3 in all cases. Regardless of the synthesis conditions, supramolecular ensembles were obtained, which was confirmed by X-ray diffraction analysis. In compound $[K(18C6)(H_2O)_{1.66}]_{2n}$ $\{[K(18C6)]_2[Sc(NCS)_6]\}_n \cdot n$Cl (**XV**), the thiocyanate ion is coordinated by scandium through the nitrogen atom to form an octahedral anion $[Sc(NCS)_6]^{3-}$. In structure **XV**, each 18C6 molecule coordinates one potassium atom, and two [K(18C6)] complexes form a dimer. The environment of the potassium atom is built up to a hexagonal bipyramid by the sulfur atom of the centrosymmetric scandium anion, resulting in the formation a chain motif (Fig. 7) [50]. Compound **XV** is isostructural to $[K(18C6)(EtOH)]_{2n}\{[K(18C6)]_2$ $[Er(NCS)_6]\}_n \cdot n$(NCS) [51] and $[K(18C6)(H_2O)_{1.25}]_{2n}$ $\{[K(18C6)]_2[Y(NCS)_6]\}_n \cdot n$(NCS) [23].

For the rare-earth metals with the small NCS ligand, octahedral anions with a coordination number of 6 are not typical: they are stabilized under the action of external effects (cations, guest molecules, supramolecular aggregation). Homoleptic forms with higher coordination numbers can be obtained by changing the synthesis conditions, except for the presence of water. For example, isomorphic compounds $[Me_4N]_4[M(NCS)_7]$ (M = Dy, Er, Yb) (**XVI**) stable in air at room temperature for several weeks were obtained in an anhydrous medium (methanol–benzene) and structurally characterized [52]. The metal atom in compound **XVI** localized at the center of the distorted pentagonal bipyramid is coordinated by seven nitrogen atoms (coordination number 7). The NYbN angle of the axial axis is 163.9°, and the average angle of the bond MNS is 176.9°. The changes in the M–N bond lengths are symbate to the variations of the ion radius and the number of the rare-earth metal.

The homoleptic complexes with a coordination number of 7 in the form of inclusion compounds $[Et_4N]_4[M(NCS)_7] \cdot C_6H_6$ (M = La, Pr) (**XVII**) were isolated from an anhydrous methanol solution kept at room temperature under C_6H_6 vapors [53]. The crystals of compound **XVII** are stable at room temperature for several weeks, and on heating they lose benzene molecules at 60°C. The central metal atom in compound **XVII** coordinates seven nitrogen atoms, and a coordination number of 7 is observed in the geometry of a one-capped trigonal prism, unlike compounds **XVI** with the pentagonal bipyramidal configuration. The stabilization of the homoleptic five-charged anion $[M(NCS)_8]^{5-}$ in structures $[Me_4N]_5[M(NCS)_8] \cdot 2(C_6H_6)$ (M = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy) (**XVIII**) and $[Me_4N]_5[La(NCS)_8] \cdot 2(C_6H_5F)$ [54] seems unusual. In isomorphic compounds **XVIII**, the metallic center is coordinated by eight nitrogen atoms of the acido ligand and a coordination number of 8 is observed in the geometry intermediate between a cube and a square antiprism. The solvate with fluorobenzene was obtained only for lanthanum, whose maximum ion radius makes it possible to obtain an inclusion compound with a more bulky C_6H_5F molecule. Interestingly, the benzene molecules are retained in structure **XVIII** (Pr) to 170°C (DTA) and are not removed even on heating at 110°C for 12 (Pr, Nd), 10 (Eu), and 6 h (Gd). Molecules of C_6H_6 in compounds **XVIII** (La, Ce, Tb, Dy) and fluorobenzene molecules in the La complex are removed completely within 2 h at 110°C.

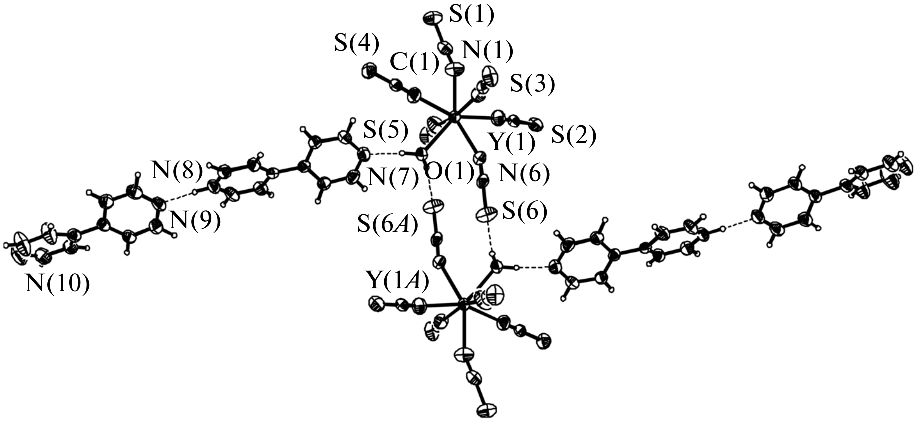

Fig. 8. Fragment of structure $[H_3(4,4'\text{-Bipy})_4][Y(NCS)_6(H_2O)]$.

Heteroleptic thiocyanate compounds. Homoleptic forms of the rare-earth metals easily transform into heteroleptic thiocyanate compounds with different degrees of aquation (solvation) and structural variety. Complexes $[Et_4N]_4[Ln(NCS)_7(H_2O)]$ (Ln = La, Ce, Pr, Nd, Dy, Er) were synthesized from lanthanide thiocyanates prepared from hydrated Ln chlorides and KNCS in methanol without solid phase isolation. The complexes were isolated after the reaction solutions were kept over silica gel [55]. The first lanthanides (La, Ce, Pr) form isomorphic cubic crystals, while Nd, Dy, and Er give another series of isomorphic tetragonal complexes. The coordination geometry does not change for both types of the complexes: the ligands form a cubic environment around Ln. A comparison of these complexes with compound **XVIII** shows that the insertion of a molecular ligand into the coordination sphere of the lanthanide metal decreases the charge of the complex to –4 with the retention of the coordination number equal to 8, but the coordination mode transforms into LnN_7O.

The aquated polythiocyanate anions of the rare-earth metals, $[Ln(NCS)_x(H_2O)_y]^{3-x}$ with $x = 6$–8, $y = 0$–2, and $x + y < 10$ for Ln = Y and La–Yb, synthesized from Ln perchlorates and NH_4NCS turned out to be successful objects for the preparation of low-melting ionic liquids based on the $[Ln(NCS)_7(H_2O)]^{4-}$ anions with 1-butyl-3-methylimidazolinium as a cation [56].

Compounds $[Me_4N]_3[M(NCS)_6(CH_3OH)(H_2O)]$ (M = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er) obtained in transmetallation reactions form a series of monoclinic isomorphic salts with the coordination number 8 and coordination mode LnN_6O_2 due to six acido ligands and two molecular ligands (CH_3OH, H_2O) forming the coordination sphere as a square antiprism with the almost axial position of the O-ligands relative to two square planes [52]. The heteroleptic three-charged anion $[M(NCS)_6(H_2O)]^{3-}$ is also present in $[H_3(4,4'\text{-Bipy})_4][Y(NCS)_6(H_2O)]$ (Fig. 8) [41]. The hexathiocyanate anions of the rare-earth metals were used for the preparation of organic semiconductors $(ET)_5[M(NCS)_6(NO_3)] \cdot C_2H_5OH$ (M = Y, Dy, Ho; ET is bis(ethylenedithio)tetrathiafulvalene). In the four-charged anions, the metallic center is coordinated by six nitrogen atoms of the thiocyanate ligands and one bidentate nitrate group (coordination mode MN_6O_2) to form a dodecahedral geometry [57].

The heteroleptic tetrathiocyanate anions are stable in salts with various cations, which affects, as a rule, the composition and geometry of the thiocyanate anion. Double salts $K_4[Ln(NCS)_4(H_2O)_4] \cdot (NCS)_3 \cdot nH_2O$ (Ln = Nd, Eu) are known; in the isostructural compounds, the anionic complex is the Archimedes antiprism with the coordination mode LnN_4O_4 [58]. Isomorphic complexes $[Et_4N][Ln(NCS)_4(H_2O)_4]$ (Ln = Nd, Eu) were obtained by keeping the reaction solution (after transmetallation) in a benzene atmosphere. The coordination mode LnN_4O_4 is observed in the geometry of a square antiprism in which the pair of oxygen atoms and the pair of nitrogen atoms are localized in the *cis* positions on the upper plane and in the *trans* position on the bottom plane, respectively [59]. In the compounds where protonated 4,4'-Bipy acts as a cation, tetrathiocyanate anions with different degrees of aquation are formed: $[H(4,4'\text{-Bipy})][Y(NCS)_4(H_2O)_3] \cdot 2(4,4'\text{-Bipy}) \cdot 2H_2O$ and $[H(4,4'\text{-Bipy})_2]_n[(\mu\text{-}(4,4'\text{-Bipy})Y(NCS)_4(H_2O)_2]$. In the monomeric and polymeric ensembles, yttrium in the anionic complexes has the coordination number 7 but different compositions of the coordination mode: YN_4O_3 and YN_5O_2 (Fig. 9) [41]. Salt $[HPz_2]_2[Y_4(NCS)_4(H_2O)_4]_2 \cdot Pz$ was obtained from a **I**–Pz(pyrazine)–HNCS solution [42], and its tetrathiocyanate anion has a coordination number of 8 and coordination mode YN_4O_4. The replacement of ditopic ligands by chelating ones, 2,2'-

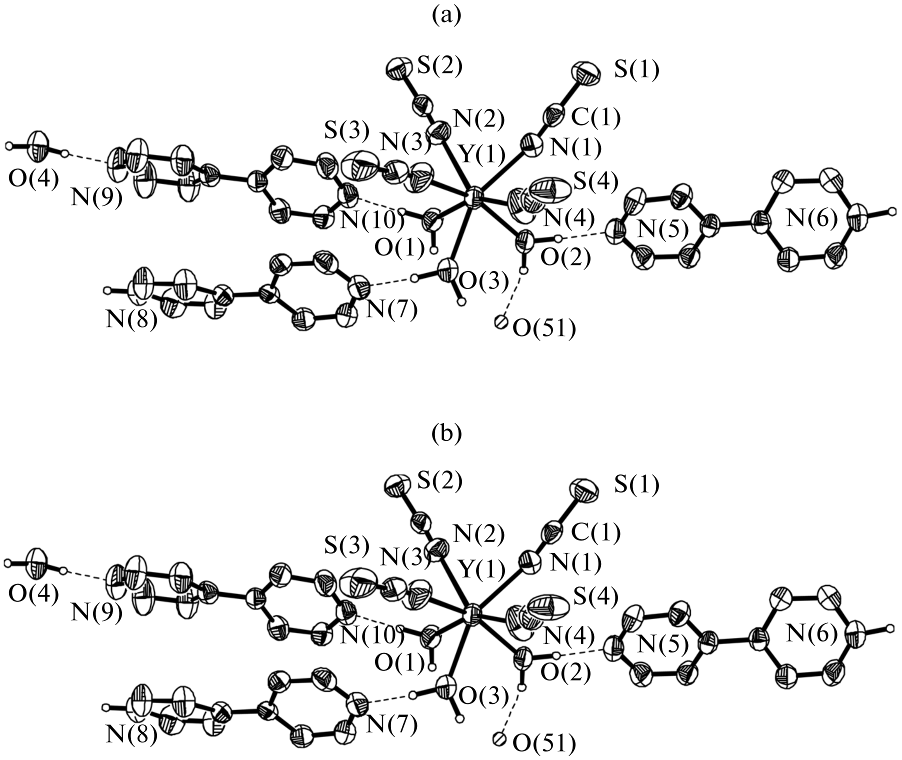

Fig. 9. Fragments of the structures of compounds (a) $[H(4,4'\text{-Bipy})][Y(NCS)_4(H_2O)_3] \cdot 2(4,4'\text{-Bipy}) \cdot 2H_2O$ and (b) $[H(4,4'\text{-Bipy})_2]_n[\mu\text{-}(4,4'\text{-Bipy})Y(NCS)_4(H_2O)_2]_n$.

bipyridine and 1,10-phenanthroline, results in compounds $[HBipy][Y(NCS)_4(Bipy)_2] \cdot H_2O$ and $[HPhen][Y(NCS)_4(Phen)_2]$ containing no water molecules in the coordination sphere. Their tetrathiocyanate anions have the coordination number 8 and coordination mode YN_8 formed of the nitrogen atoms only. Four of them are presented by acido ligands, and four other nitrogen atoms are presented by two molecules of the N-heterocycle. In the coordination with the bidentate ligands, protonated and coordinated diimines simultaneously participate in stacking interactions [60].

Molecular ligands vary the aquation of the thiocyanate complexes and also induce the displacement of the acido ligand to the external coordination sphere. According to the X-ray diffraction data, the cationic thiocyanate complex is formed by the coordination of heptadonor polyglycol EO_6 and the replacement of one thiocyanate anion by a water molecule, and the central metal atom in compounds $[M(NCS)_2(H_2O)(EO6)] \cdot (NCS)$ ($M = La$, Ce) has the coordination number 10 and coordination mode MN_2O_8 [28]. Thiocyanate ions are also displaced from the first coordination sphere of yttrium in the reactions of compound **I** with ditopic 4,7-Phen in ethanol solutions to give ensemble $[Y(H_2O)_7(NCS)](NCS)_2 \cdot 5(4,7\text{-Phen}) \cdot 5(H_2O)$. In the monomeric dicationic complex of this ensemble, the coordination number of yttrium is 8, the coordination mode is YNO_7, the yttrium polyhedron is a square antiprism, and the transition of molecular complex **I** to the dicationic complex occurs without changing the coordination number of the metal [42].

The formation of ionic complexes from thiocyanates (halides) of hard cations via the autocomplexation (disproportionation) reaction $2MX_3 \rightarrow MX_2^+ + MX_4^-$ has been known long ago [61]. This process is determined by many factors, the main of which are the steric characteristics and the donor ability of the competing ligands. For example, isostructural associates $[Sc(H_2O)_4(NCS)_2][Sc(H_2O)_2(NCS)_4] \cdot 2(18C6)$ **(XIX)** and $[Sc(H_2O)_4(NCS)_2][Sc(H_2O)_2(NCS)_4] \cdot 3(18C6) \cdot H_2O$ **(XX)** formed by cations $[Sc(H_2O)_4(NCS)_2]^+$, anions $[Sc(H_2O)_2(NCS)_4]^-$, and crown ether **(XIX)** and water **(XX)** molecules were synthesized for scandium. The cations form sandwiches with the macrocycle molecules (Fig. 10), and the anions form chains (Fig. 11). Regardless of the charge of the complex, scandium has a coordination number of 6 in both anions and cations [62]. The autocomplexation reaction appeared especially clearly for the synthesis of ensemble $Eu_3(H_2O)_{12}(EtOH)_3(NCS)_9$ **(XXI)** [24].

Structure **XXI** is formed by complexes of three types: molecular $[Eu(H_2O)_4(EtOH)(NCS)_3]$, cationic $[Eu(H_2O)_4(EtOH)_2(NCS)_2]^+$, and anionic $[Eu(H_2O)_4(NCS)_4]^-$. The coordination number of Eu atoms in all complexes is 8, the polyhedra are tetragonal antiprisms with different degrees of distortion, and 27 hydrogen atoms of the coordinated water and EtOH molecules join the complexes into a 3D structure by hydrogen bonds (Fig. 12). Hard cations tend to form complexes with a maximum number of ligands similar in donor characteristics. This took place in the case of aquaethanol europium thiocyanate $[Eu(H_2O)_4(EtOH)(NCS)_3]$: six (of eight) molecular ligands (H_2O and EtOH) in the cationic complex, and four NCS anions and four H_2O molecules in the anionic complex. Regardless of the position of the rare-earth metal in the Group, easiest Sc and heavier Eu in ensembles **XIX–XXI** are presented by the cationic and anionic thiocyanate complexes.

To conclude, the variety of the structural chemistry of rare-earth metals depends on the donor ability of the ligands and solvents used, which affects the formation of various forms: molecular, ionic monomeric, and oligomeric complexes. Even insignificant changes in the ligand environment can dramatically modify the physical properties of the rare-earth metal compounds. The formation of the first and second (external) coordination spheres in the complexes and supramolecular association depend on the secondary interactions caused by the ligands and solvents. This was clearly demonstrated for the influence of the solvent on the formation of the thiocyanate complexes of Y, Eu, and Tb with 18C6 [23, 24, 30] and the supramolecular ensembles of yttrium thiocyanate with 4,4'-Bipy and 4,7-Phen [41, 42] and for a decrease in the coordination number of yttrium to 7 in the supramolecular ensembles with 18C6 and ditopic 4,4'-Bipy. The influence of the synthesis conditions, medium, and cation is observed for the variations of the coordination number (from 6 to 10), the number of thiocyanate ligands (and, correspondingly, the charge state), and the geometry of the coordination sphere in the homo- and heteroleptic ionic thiocyanate complexes (Table 2). Heteroleptic tetrathiocyanate anions are stable in salts with various cations, which influence, as a rule, on the composition and geometry of the thiocyanate anion [41, 42, 58, 59]. The ensembles combining cationic and anionic complexes of one complexing agent with the same coordination number are of special interest [24, 62].

The recent studies of the thiocyanate compounds of the rare-earth metals revealed several applied directions of using these complexes. The preparation of ionic liquids with thiocyanate anions provides new possibilities for the formation of compounds with interesting luminescence properties and good photo-

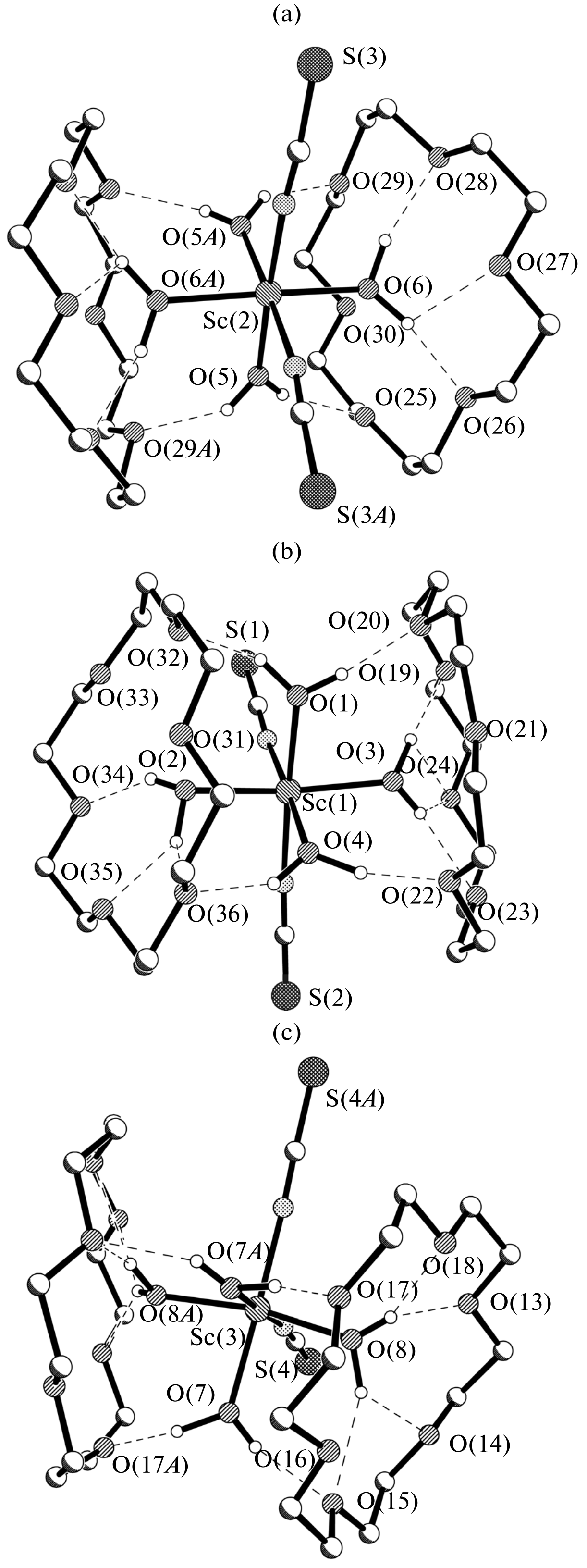

Fig. 10. Structure of cations $[Sc(H_2O)_4(NCS)_2]^+ \cdot 2(18C6)$ in compound $[Sc(H_2O)_4(NCS)_2][Sc(H_2O)_2(NCS)_4] \cdot 3(18C6) \cdot H_2O$.

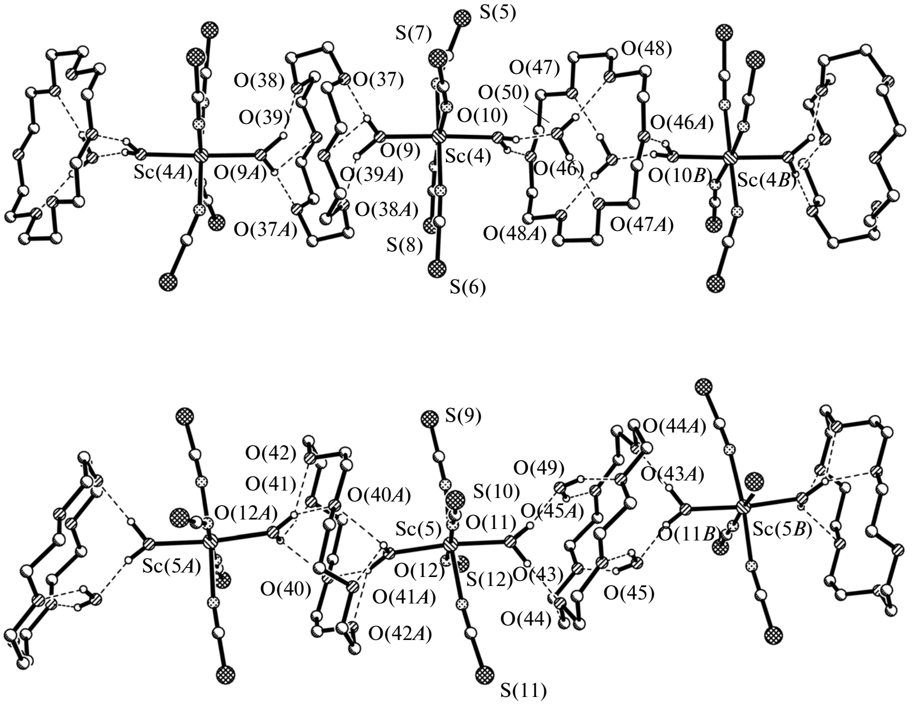

Fig. 11. Structure of chains $[Sc(H_2O)_2(NCS)_4](18C6) \cdot H_2O$ in compound $[Sc(H_2O)_4(NCS)_2][Sc(H_2O)_2(NCS)_4] \cdot 3(18C6) \cdot H_2O$.

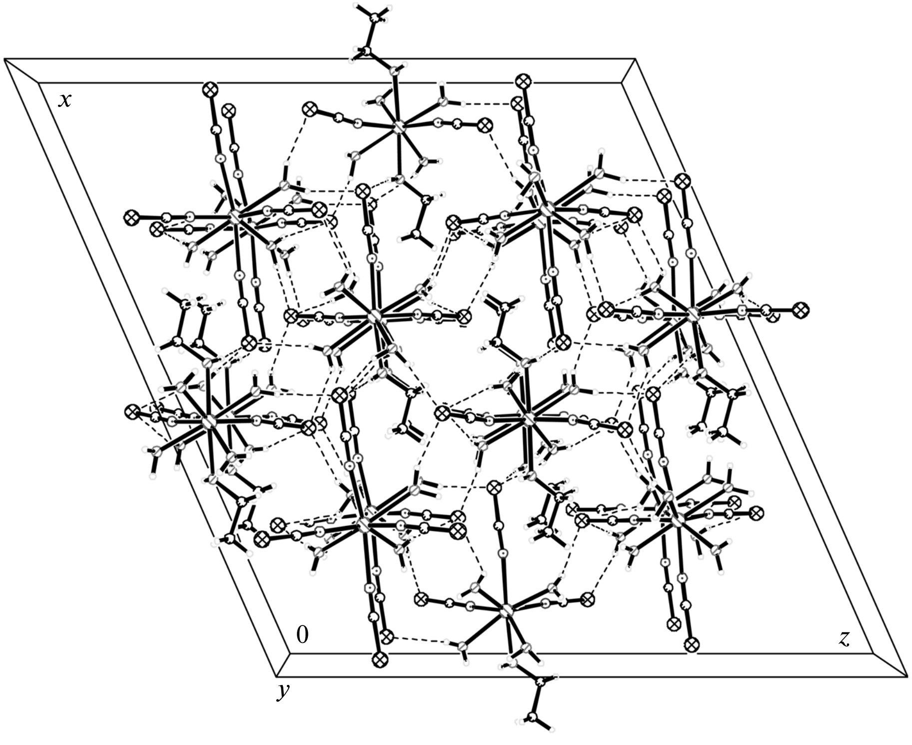

Fig. 12. Projection of the $Eu_3(H_2O)_{12}(EtOH)_3(NCS)_9$ structure on the plane (010).

chemical stability. The synthesis of the thiocyanate lanthanide compounds with N-heterocycles, which along with NCS^- anions increase the luminescence intensity (antenna effect) of the lanthanide complexes, is of practical interest. An increasing use is observed for the coordination compounds of rare-earth metals as contrast substances and luminescent indicators in medical diagnostic studies and as antioxidants and antitumor remedies exhibiting cytotoxicity toward various types of cancer cells in therapy.

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